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L. J. Wood

The Effect of Cerium Alloy on the
Properties of Cast Iron

THE EFFECT OF CERIUM ALLOY ON THE
PROPERTIES OF CAST IRON

BY

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THESIS

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY
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BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR
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TABLE OF CONTENTS

	Page
Acknowledgment	
Introduction	1
Johnson's Solution Theory of Oxygen	1
The Compound Theory of Oxygen	2
Deoxidizers	3
Method of Treatment	6
Analysis	11
Sulfur	12
Phosphorus	14
Manganese	15
Silicon	16
Graphite	17
Cerium	19
Reagents Used	19
Microphotographs	21
The Work of Photographing	21
Physical Tests	27
Transverse Test	28
Tensile Test	28
Hardness	29
Summary	42
Conclusions	44
Suggestions for Further Work	44

LIST OF ILLUSTRATIONS

	Page
Sulfur Apparatus	13
Carbon Train	18
Microphotographs	22-26
Graphical Physical Test Data	30-40

THE EFFECT OF CERIUM ALLOY ON THE PROPERTIES OF CAST IRON

I INTRODUCTION.

For a long time it has been known that small amounts of impurities in cast iron have a very marked effect on its properties such as hardness, tensile strength and cross-breaking strength. The exact magnitude of these effects, how they vary with the impurity and how they can best be controlled has been a matter of a very large amount of study and experiment. The effects of most of the common constituents are fairly well understood and can be reasonably well controlled. There is, however, one very common component from which cast iron is probably never entirely free but which may have a considerable influence upon it. This element is oxygen.

It is difficult to know very much about the effect of oxygen on the properties of cast iron since there seems to be no very good quantitative method for its analysis and in the second place, up to the present time no one has been able to prove the condition of oxygen in iron. Some believe that it exists as an oxide of iron, others as an oxysulfide but there is little or no evidence for either of these beliefs and there are many other possibilities. Altho there are many theories concerning the state of existence of oxygen in iron most of them can be classed under one of two general heads.

Johnson's Solution Theory of Oxygen.

Mr. J. E. Johnson, Jr., now deceased, after some six years of work on the problem states that oxygen in iron increases its desirable properties since it causes a segregation or

spherodizing of the graphite. Graphite in this form rather than in the large flaky condition most often seen, would not separate so many crystals of iron and in this way would increase its strength. A complete discussion of the theory may be found in the "Transactions of the American Institute of Mining Engineers".

The Compound Theory of Oxygen.

The second of these general theories holds that the oxygen present, exists as an oxide, oxysulfide or some other compound which neither dissolves in nor alloys with the iron but forms a more or less continuous network thru it, placing the crystals in small individual film-sacs or perhaps stretching its fibrous network along the cleavage planes themselves. This is a very reasonable supposition since sulfur is known to do this very thing and oxygen and sulfur are very closely related in the periodic system of grouping. If this theory is true the presence of any considerable quantity of oxygen would undoubtedly be very detrimental to the properties of the iron. Working on this idea many elements have been used as deoxidizers, some of the more common being manganese, silicon, aluminium, titanium and vanadium. Oxygen compounds will be formed with these elements more easily than with iron. If the deoxidizer is effective the oxygen compound will either be removed as slag or form small segregated masses of material which will neither dissolve in the iron nor be alloyed with it. This theory is greatly strengthened by the fact that sulfur, the relative of oxygen, is known to act in this manner when sufficient manganese is present in the molten iron. The compound theory of oxygen is supported by metallographists such as Howe, Sauveur and Stoughton.

There is really nothing contradictory in these two theories and it is possible that both may be correct at least to some extent. It is, however, extremely difficult to determine whether either, both or neither of the theories are correct because, as pointed out above, no reliable, quantitative analytical method for oxygen is known and in the second place because any excess of the deoxidizer may alloy with the iron and thus cause a variation in its properties.

II DEOXIDIZERS

There has been a large number of substances used as deoxidizers some of which have been mentioned above such as manganese, silicon, aluminium, titanium and vanadium. New substances are constantly being tried for the purpose of deoxidation with more or less success. Possibly the latest of these substances or at least one of the latest is mich metal, an alloy of cerium earth metals. The mixture usually contains about 55 per cent of cerium, 15 per cent of lanthnum, and the remainder of didymium and samarium and probably other rare earth metals of the cerium group. This mixture has been alloyed with iron in the proportion of three to seven and placed upon the market under the trade name of "Cela iron" as a deoxidizer of iron. In the remainder of this article this alloy will be known as cerium or cerium alloy and any percentages given will refer to percentages of rare earth metals, the per cent of iron alloyed with it being cared for in the calculation.

The first work to be published on the use of cerium as a deoxidizer in cast iron was a paper, "Cerium in Cast Iron", presented by Dr. Richard Moldenke at the September 29,

1919 meeting of the American Foundrymen's Association. Dr. Moldenke mentioned briefly the use of deoxidizers in cast iron and then described the properties and methods of production of cerium as the latest addition to the list of deoxidizers. He also gave the results of a series of tests which he ran in his own foundry using cerium as a deoxidizer. A short summary of his work follows.

Tests were run of three types of iron, sixteen standard 1 1/4 inch round test bars being cast from each type, and three sets of four bars treated with .05, .10 and .15 per cent cerium. The bars were cast in cores with a top pour. The metal was treated with the cerium in the ladle, the weight of the alloy being such that the correct amount of cerium was added. His first iron was an all pig iron mixture with an analysis of silicon 2.7, sulfur .07, manganese .60, phosphorus .64. His second iron was a part pig and part scrap mixture containing 2.4 per cent silicon, .10 per cent sulfur, .55 per cent manganese and .68 per cent phosphorus. The third iron was from a remelted car wheel charge with an analysis of .55 per cent silicon, .13 per cent sulfur, .40 per cent manganese, and .40 per cent phosphorus. The bars were subjected to a cross-breaking test and the deflection and breaking load recorded. The following is a summary of the data obtained, giving transverse strength and deflection.

o/o Ce	I		II		III	
	T. S.	Dflec.	T. S.	Dflec.	T. S.	Dflec.
.000	2090	.11	2740	.09	3970	.11
.050	2450	.12	3110	.10	4080	.14
.100	2660	.13	3240	.11	4190	.15
.150	2840	.13	3280	.13	Bars defective	

These tests show a marked increase in transverse strength on the addition of small quantities of cerium. Dr. Moldenke explained these results by means of his theory of oxygen

in cast iron. Briefly this theory holds that dissolved oxygen in iron forms an oxide which raises the freezing point of the molten metal to a considerable extent. It farther states that the presence of oxygen also tends to increase the percentage of cementite thus making the iron more difficult to machine. In the third place Dr. Moldenke holds that dissolved oxygen in cast iron tends to form gases. He explains the increased strength of the cerium samples, as shown on page 4, by saying that the cerium has removed, at least a part of the oxygen, and hence has avoided the evils of cold iron, excess cementite and the formation of a certain amount of gas in the molten metal. Reference was made in this same article to tests made with this deoxidizer at the Chicago Hardware Company Plant but as this data was unavailable no further reference will be made to it.

Dr. Moldenke's report is very interesting but he has given very little experimental evidence upon which to base such definite conclusions. Most of his evidence seems to be based on the results of a few cross breaking tests and the appearance of a few fractures. Not a single microphotograph was shown. It has been the purpose of this work to make cerium treatments of iron as described above and an effort has been made to accumulate data which might make it possible to draw conclusions from a little firmer experimental basis or in other words to answer the following questions:

1. Does the addition of cerium to cast iron cause any change in any of its properties?

2. If there there is a change would the use of cerium in this way be possible economically?

METHOD OF TREATMENT

It is obvious that if metallic cerium does have such a pronounced beneficial effect on the properties of cast iron the problem is well worth a considerable amount of time and study. It will be necessary to determine, as nearly as possible, what changes take place and how these are best brought about. It is entirely possible that either good or bad influences might be exerted, depending upon the method of treatment. In actual practise in industry this difficulty of treatment will become increasingly greater since an effective method may tend to cause a deterioration of some other desirable property. There are at least two general ways in which the cerium may be added. In the first place it may be added to the charge before melting or in the second place to the molten metal after coming from the cupola. The first method would probably not be feasible since it is very likely that much of the cerium would be lost in the cupola. This would make the process prohibitive since cerium is a relatively expensive product, especially for industrial purposes. The second method however seems to present a possibility.

In this research the cerium alloy was added directly to the molten metal or rather was placed in the bottom of the ladle and the molten iron poured upon it. If the alloy is added to the surface of the iron the reaction is very violent even if only a very small amount is used such as .2 to .3 per cent. Besides being to an extent dangerous there is a probability that a considerable amount of the cerium is lost. So, with only two or three exceptions the cerium alloy was placed in the ladle before the molten iron.

Even to this method of treatment there is a rather serious objection. Every foundryman knows the evils of "cold iron" and it is evidently impossible to treat and thoroly mix the iron without a considerable fall in temperature. However if the iron is very hot when tapped from the cupola this objection can be largely overcome. Especially would this be true if the treatment were practised on a commercial scale since a definite volume rather than weight could be treated thus saving the time required for weighing and also a much larger amount could be treated than was possible in this research. These two considerations would eliminate, almost entirely the objection mentioned in the beginning of this paragraph.

In this work fifty pound quantities of iron were treated with amounts of the cerium alloy, varying from .1 to .6 per cent; most of the treatments varying within the limits of .1 to .25 per cent. A ladle, previously heated, was weighed and the weighed sample of cerium dropped into it immediately before pouring in the iron. In this way a definite percentage could be obtained with a considerable degree of accuracy. The iron was stirred thoroly, as rapidly as possible, and poured into standard test bar molds. The iron for the various treatments was as nearly uniform as could be obtained under the prevailing conditions of operation in the university foundry. In each case an untreated set of bars was cast thus making it possible to compare the results, not only from bars of various percentage treatments but also from untreated iron of the same cast. These comparisons were made by means of a large number of tests of various kinds including quantitative analysis, several different physical tests such as

cross-breaking strength, tensile strength and hardness. Besides these tests a large number of microphotographs were taken.

The bars used were standard 1 1/4 inch, round test bars. They were cast on end in dried sand molds with a top pour. The molds used in the first part of the work were rammed by hand but this method was found to be unsatisfactory and the remainder were rammed by a jar ramming machine after which they were thoroly dried in oil fired ovens. A small amount of sea coal facing was used with the molding sand for the purpose of giving a smooth finish to the bars. After casting, the bars were allowed to cool in the molds for a day and then were "shaken out", brushed and marked on the ends. In all some 140 bars were cast of which number all but 88 were discarded because of defects due to foundry practise. Most of the defects in the rejected bars were caused by improper ramming altho a few at the first were caused by wet sand.

The samples are divided into six separate casts. The cupola charges from the various casts were as follows.

Cast A. Part pig iron and part scrap steel, a standard mixture used at Burr's Foundry, Champaign Illinois. The bars were cast in green sand molds. Trouble was experierced with cold iron in the higher treatments due to delay in weighing.

Cast B. Part pig and part scrap iron. Eight bars were cast of each treatment, four in dry and four in green sand molds. The green sand molds were rammed too hard which caused a loss of twelve bars by blowing.

Cast C. An all scrap charge poured at the Mechanical Engineering Open House. Trouble was experienced with cold iron.

Cast E. Part pig and part scrap iron poured very hot. Poor molds caused the loss of several bars.

Cast F. Part pig and part scrap iron poured hot. Several over dried molds gave pitted bars.

Cast G. Part pig and part scrap iron cast fairly hot. A set of over dried molds caused a very heavy loss of bars.

The various casts are divided into "treatments", there being for the most part four treatments in a cast. An effort was made to have the chemical composition of each cast as nearly uniform as possible except for the addition of the cerium alloy. The table below shows the entire number of samples divided into their proper casts and "treatments". It also shows the date and place of casting along with the individual specimen markings. These samples will be kept at the University of Illinois and may be identified by means of these marks.

Table I

Cast	o/o Ce	Date	Place	Specimen
		cast	cast	markings
A-1-a	00.00	12/11/'19	Burr's	...
2	"	"	"	...
1-b	0.10	"	"	...
2	"	"	"	...
1-c	0.15	"	"	...
2	"	"	"	...
1-d	0.25	"	"	...
2	"	"	"	...
B-1-a	0.00	3/16/	U. of I.	10
2	"	"	"	11
3	"	"	"	12
4	"	"	"	13
5	"	"	"	14
6	"	"	"	15
7	"	"	"	16
8	"	"	"	17
1-b	.10	"	"	20
2	"	"	"	21
3	"	"	"	22
4	"	"	"	23
1-c	.15	"	"	30
2	"	"	"	31

Cast	o/o Ce	Date cast	Place cast	10 Specimen
				markings
B-3-c	0.15	3/16/1920	U. of I.	32
4	"	"	"	33
1-d	0.25	"	"	40
2	"	"	"	41
3	"	"	"	42
4	"	"	"	43
C-1-a	0.00	3/23/1920	"	24
2	"	"	"	25
3	"	"	"	26
4	"	"	"	27
5	"	"	"	28
6	"	"	"	29
1-b	0.10	"	"	34
2	"	"	"	35
3	"	"	"	36
4	"	"	"	37
1-c	0.15	"	"	44
2	"	"	"	45
3	"	"	"	46
4	"	"	"	47
1-d	0.25	"	"	50
2	"	"	"	51
3	"	"	"	52
4	"	"	"	53
D-1-a	0.00	4/8/1920	"	18
2	"	"	"	19
E-1-a	0.00	"	"	38
2	"	"	"	39
1-b	0.10	"	"	48
2	"	"	"	49
1-c	0.15	"	"	57
2	"	"	"	54
1-d	0.25	"	"	55
3	"	"	"	56
F-1-a	0.00	4/15/1920	"	58
2	"	"	"	59
1-b	0.10	"	"	60
2	"	"	"	61
3	"	"	"	62
4	"	"	"	63
1-c	0.15	"	"	64
2	"	"	"	65
3	"	"	"	66
4	"	"	"	67
1-d	0.25	"	"	68
2	"	"	"	69
3	"	"	"	70
1-a	0.40	"	"	71
2	"	"	"	72
3	"	"	"	73

Cast	o/o Ce	Date	Place	Specimen
		cast	cast	markings
G-1-a	0.00	4/22/1920	U. of I.	74
2	"	"	"	75
1-b	0.10	"	"	78
2	"	"	"	79
3	"	"	"	80
4	"	"	"	81
1-c	0.15	"	"	82
2	"	"	"	83
3	"	"	"	84
4	"	"	"	85
1-d	0.25	"	"	86
2	"	"	"	87
1-e	0.60	"	"	90
2	"	"	"	91
3	"	"	"	92
4	"	"	"	93

Note. "Burr's" means Burr's Foundry of Champaign Illinois.

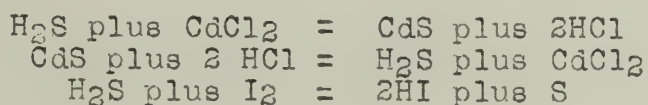
This table will be referred to in the remainder of this thesis as the "Sample Index" table.

ANALYSIS

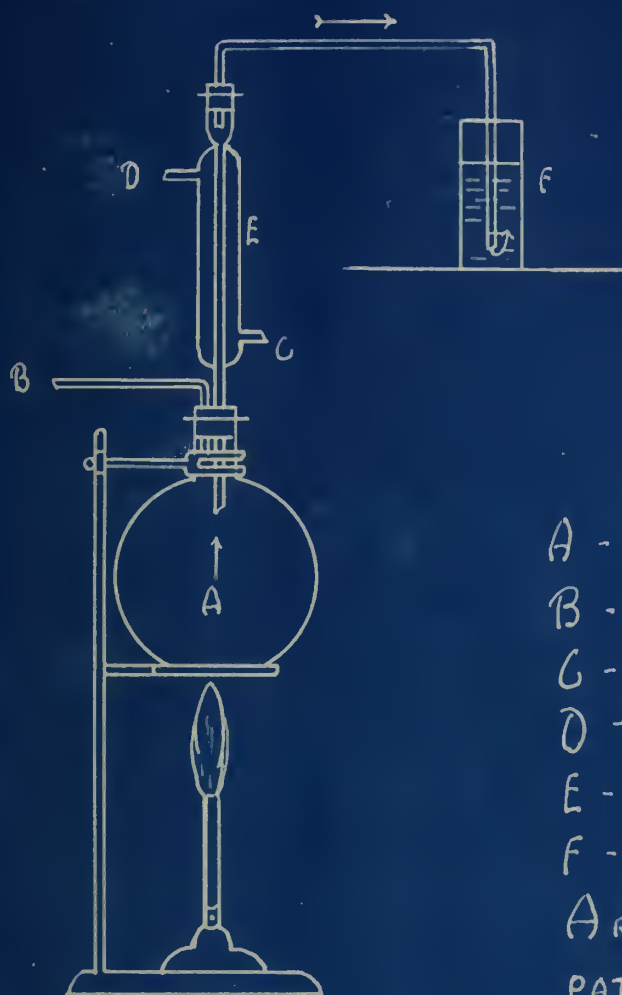
Since this research is for the purpose of detecting any variation in the properties of cast iron when treated with cerium and since it is well known that the constituents or impurities of the iron have a very direct influence upon its properties, it is necessary to know the composition of the iron before and after treatment. Even if the composition remains constant after treating with cerium it does not necessarily follow that no changes in the properties of the iron have taken place. However if the composition has varied some change in properties may reasonably be looked for. Quantitative analytical tests were made for sulfur, phosphorus, manganese, silicon, graphite and cerium. It might be well, at this time, to describe briefly the analytical methods used, thus making it possible for any future investigators to check the work by the same analytical methods.

Sulfur.

The sulfur was evolved from a hydrochloric acid solution of the sample as hydrogen sulfide, this being absorbed in a cadmium chloride solution and precipitated as cadmium sulfide. The cadmium sulfide was dissolved in hydrochloric acid and the resulting hydrogen sulfide was titrated against standard iodine. This method is known as the hydrogen sulfide method for the determination of sulfur. To be more specific, 5 grams of sample were placed in the flask A as shown in figure 1. About 30 cc of cadmium chloried solution and 40 cc of water were placed in the cylinder F and all of the connections made as shown in the drawing. Cold water was circulated thru the condenser E, the purpose being to allow the hydrogen sulfide gas to pass off as pure as possible by condensing as much steam and other impurities as possible. When all was in readiness 100 cc of hydrochloric acid(Sp Gr 1.1) was added thru the condenser. When the reaction in flask A became slower the solution was boiled gently as long as any hydrogen sulfide gas was given off. Then by removing the glass tip from the tube B and blowing into it, practically all of the residual hydrogen sulfide was forced into the cadmium chloride cylinder. This precipitate was then dissolved in strong hydrochloric acid (Sp. Gr. 1.42) and the resulting hydrogen sulfide was titrated against standard iodine; fresh starch solution being used as an indicator. The reactions of the determination are as follows.



This is a very rapid, fairly accurate method for the estimation of sulfur. Good results ought to be obtained if the above directions are followed closely.



A - HCl.

B - Air.

C - INLET FOR H_2O .

D - OUTLET FOR H_2O .

E - CONDENSER.

F - $CdCl_2$

ARROWS INDICATE THE
PATH OF H_2S .

APPARATUS FOR DETERMINATION OF S.

Phosphorus.

The phosphorus was precipitated from a nitric acid solution, presumably as ammonium phosphomolybdate. This precipitate, after being washed, was dissolved in an excess of standard sodium hydroxide and the excess titrated against standard nitric acid. This method for the determination of phosphorus is used by the American Rolling Mills Company and was adopted almost without change. The first part of the method has been recognized as standard practise for a long time, while the last part tho not so generally used is still a reliable method and well within the range of accuracy of ordinary analytical work. The following specific directions will outline the method more clearly.

Three grams of sample were dissolved in 60 cc of nitric acid (Sp. Gr. 1.2) and the solution concentrated to a thick syrup to oxidize the silicon. The insoluble residue was filtered on ashless filter paper and saved for the determination of silicon. The filtrate was treated with 4 to 6 cc of saturated potassium permanganate solution and heated gently until manganese dioxide was formed. Hydrochloric acid was then added and the mixture heated until solution took place. (Any insoluble material at this point will probably be graphite and should be filtered off.). The solution was made slightly alkaline with ammonia and then slightly acidic with nitric acid. The chief purpose of the neutralization with ammonia was to insure an excess of NH_4 ions in solution for the precipitation with molybdate solution. While the solution was still warm an excess of molybdate solution was added slowly with constant stirring. A temperature of about 80° and ample time were found to be very important factors in effecting a complete

precipitation of the phosphorus. After having been treated in this way the precipitate could be filtered out with ease and rapidity. The formula for the precipitate of phosphorus is probably $(\text{NH}_4)_3\text{12MoO}_3\text{PO}_4$. There are two very possible sources of error in the method. In the first place great care must be used to precipitate all of the phosphorus and in the second place the ammonium phosphomolybdate precipitate must be washed thoroly since any nitric acid remaining on the paper would require an undue amount of the standard sodium hydroxide.

Manganese.

The manganese was oxidized in a nitric acid solution to permanganic acid by means of sodium bismuthate.. A small amount of potassium nitrite was added and then 10 cc of nitric acid (Sp. Gr. 1.42) and 1/2 gram more of the sodium bismuthate. After allowing to stand for 15 minutes the solution was filtered and the filtrate titrated against standard sodium arsenite. More accurate results might be obtained if the solution were boiled with sodium bismuthate until manganese dioxide formed, decomposing this with potassium nitrite and adding more nitric acid and sodium bismuthate, yet the method first described gives good results and also avoids one possible source of error. The method is generally known as the sodium bismuthate method for manganese but has been considerably modified for the present work. More specific directions are as follows.

Dissolve 1 gram of sample in boiling nitric acid (Sp. Gr. 1.2) and filter off the insoluble residue saving this for the graphite determination. After the solution has been allowed to cool for 15 minutes add an excess of sodium bismuthate (a

little practise will enable one to determine when an excess has been added) and .1 gram of potassium nitrite. After the reaction has cease add 10cc of nitric acid (Sp. Gr. 1.42) and 1/2 gram more of sodium bismuthate. Allow the mixture to stand for 15 minutes and filter. Wash the precipitate repeatedly with nitric acid(1:3) and titrate against standard sodium arsenite at once. The disappearance of the characteristic potassium permanganate color indicates the end point. The potassium nitrite supplies any potassium that might be needed and affords an opportunity for a more complete oxidation. The potassium permanganate is reduced by the sodium arsenite.

There are two possible sources of error. First the manganese must all be oxidized and second, permanganic acid is unstable in warm nitric acid, hence the reason for cooling. This is very important and can not be overlooked. Good results were obtained by this method.

Silicon.

To determine the silicon a nitric acid solution of the sample was evaporated to a thick syrup as described under phosphorus and water added and filtered. The insoluble residue was ignited and the ignition product was weighed as silicon dioxide from which the silicon was calculated.

Place the insoluble residue from the phosphorus estimation in a beaker and add 15 to 25 cc of hydrochloric acid (Sp. Gr. 1.19) and boil for several minutes, dilute and filter. The precipitate is ignited at about 850° for about 30 minutes in a weighed porcelein dish. The dish is cooled in a dessicator and weighed. The chief source of error is in failing to get all of

the iron dissolved out of the silicon dioxide residue. It is for this reason that the first residue is boiled with hydrochloric acid. Even then some iron is sometimes left in the residue and is not found until the final ignition product is weighed. If it should be found at this point, the ignited product is treated as before which will be almost certain to eliminate the difficulty.

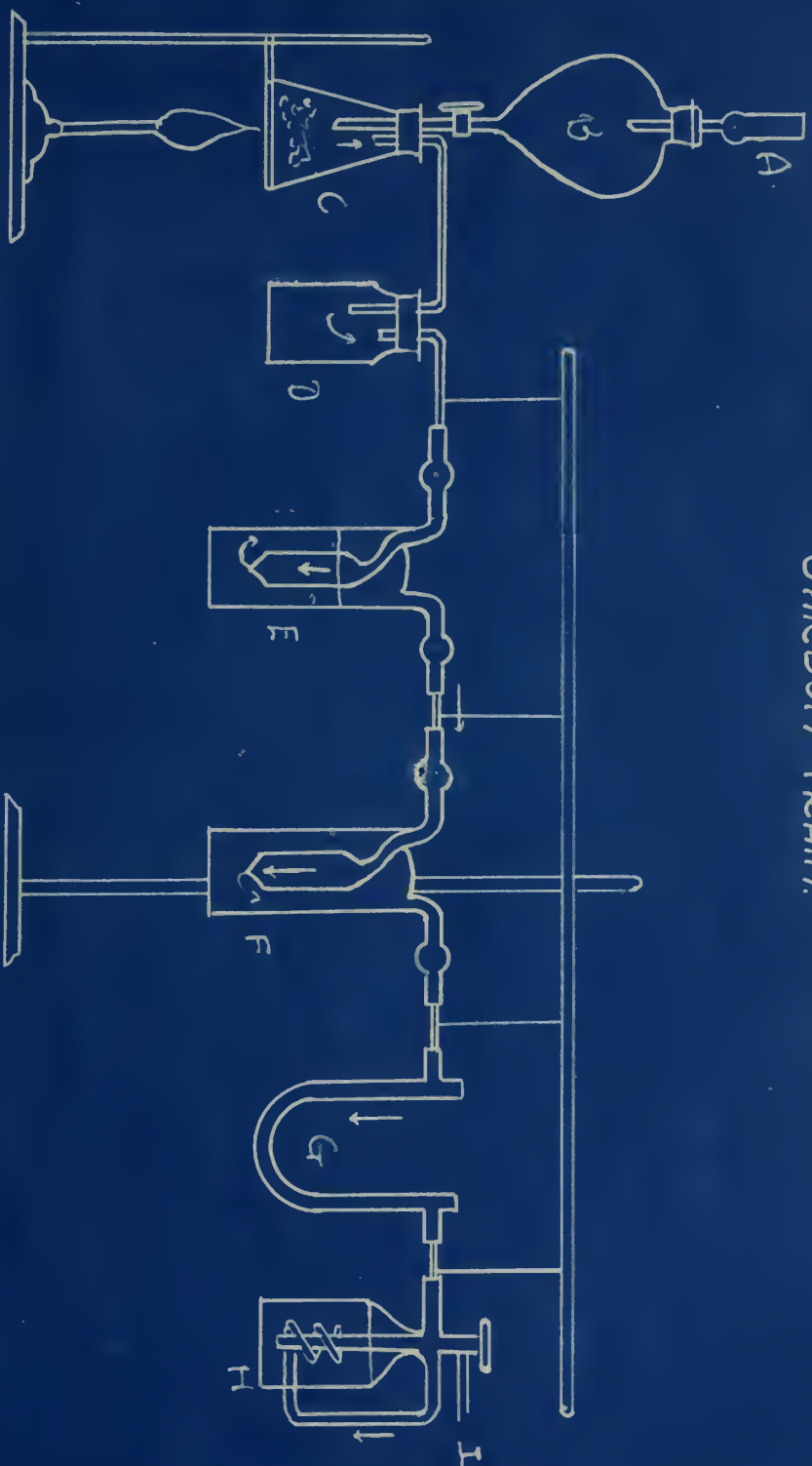
Graphite.

To determine the graphite the insoluble residue from a nitric acid solution of the sample was treated with a mixture of chromic and sulphuric acids and heated, the resulting carbon dioxide being absorbed in caustic alkali and weighed.

Place the insoluble residue from the nitric acid solution of the manganese determination in the flask C of the carbon train as shown in figure 2 and add 15 grams of chromic acid. Arrange the train as illustrated, placing the proper reagents at the proper places. Place 10 cc of sulfuric acid in the funnel B. Now open the potash bulb and apply a slight suction, just enough to draw air slowly thru it. Make all the connections and allow all of the sulfuric acid to enter flask C. If the pressure of the carbon dioxide becomes too great to allow this close the stop cock and wait until the pressure has been diminished sufficiently. Finally heat slowly to boiling and continue to boil gently until the bubbles passing thru the train are extremely few. Carefully open the stop cock of the funnel B and allow air to pass thru the train for 3 or 4 minutes. Close the potash bulb before doing anything else and remove it from the train.

There are two precautions that must be rigidly followed. First any considerable amount of water in flask C will cause the the acids to oxidize less efficiently and second there

CARBON TRAIN.



- A - KOH
 B - H_2SO_4
 C - CrO_3 : Graphite
 Arrows indicate path of CO_2
 D - Condenser.
 E - H_2SO_4
 F - Air.
 G - $CaCl_2$
 H - Vanier Bulb
 I - Suction

must be an excess of chromic acid. A little practise will enable one to estimate an excess very easily.

Cerium.

The following method for the estimation of cerium was outlined by Dr. B. S. Hopkins of the University of Illinois.

Dissolve 5 grams of sample in 100 cc of hydrochloric acid (Sp. Gr. 1.1) and neutralize with sodium hydroxide. Make the solution slightly acid with hydrochloric acid and precipitate the cerium with oxalic acid. Filter, wash and ignite the precipitate and redissolve in hydrochloric acid. Reprecipitate and ignite in the manner just described and again repeat the same operation. This repetition is to insure the complete elimination of all iron. Weigh the ignition product as ceric oxide. No cerium was found.

Reagents Used.

1. Sodium hydroxide approximately 0.15 N, each cubic centimeter of this solution used in the estimation of phosphorus being equal to approximately .0001137 grams of phosphorus.

2. Standard nitric acid approximately 0.15 N, its strength being known in cubic centimeters of the standard sodium hydroxide solution.

Sodium arsenite solution, 2 grams of arsenous acid dissolved in the least amount of hot sodium carbonate solution and this diluted to 2000 cc. One cc of this reagent used in the estimation of manganese is approximately equal to .000338 grams of manganese.

4. Potassium permanganate solution, 0.0632 N to titrate against any accidental excess of sodium arsenite solution

in the manganese determination.

5. Saturated solution of oxalic acid.

6. Standard iodine solution, 8.4 grams of iodine and 20 grams of potassium iodide dissolved in 50 cc of water and diluted to 2000 cc. One cc of this solution used in the sulfur determination is equal to approximately .00051066 grams of sulfur. (Note. This solution must be made up in the same order as directed)

7. Sodium thiosulfate to titrate against any accidental excess of iodine solution in the determination of sulfur.

8. Cadmium chloride solution, 50 grams of cadmium chloride (or 70 grams of cadmium sulfate), 500 cc of water and 1200 cc of ammonium hydroxide (Sp. Gr. 0.90), made up to 2500 cc.

9. Molybdate solution, 60 grams of molybdic oxide (MoO_3) in 440 cc of water and 60 cc of ammonium hydroxide (Sp. Gr. 0.90), poured into 500 cc of cold nitric acid (Sp. Gr. 1.2). Allow the solution to stand in a warm room for several days. Decant or filter before using.

(Note. Be sure to follow directions in the order given.)

Analytical Results.

The following table shows the results obtained from the analytical work.

Cast	Graphite	Silicon	Manganese	Sulfur	Phos.	Cerium
A-a-1	1.53	1.80	.371	.1143	.45	0.00
2				.1242	.47	"
b-1				.1118	.56	"
2				.1230	.48	"
c-1				.1205	.48	"
2				.1080	.45	"
d-1				.1006	.49	"
2	1.41	1.80	.368	.1229	.49	"

Cast	Graphite	Silicon	Manganese	Sulfur	Phos.	Cerium
B-a-1	2.5	2.2	1.15	.0653	.20	0.00
d-2	2.5	2.1	.4997	.0714	.24	"
C-a-3	2.3	1.8	.32	.1102	.32	"
d-1	2.2	1.7	.40	.0980	.29	"
D-----No Treated Specimens.						
E-a-1	1.9	1.9	1.40	.0674	.31	"
d-2	1.9	1.7	1.30	.0582	.32	"
F-a-1	2.2	1.7	.28	.0863	.7489	"
e-3	2.6	1.6	.33	.0898	.9975	"
G-a-2	2.8	1.7	.41	.1021	.23	"
e-4	2.6	1.8	.69	.0868	.24	"

(Note. The "a" treatments in each are the untreated samples.)

There is little that can be said of the relationship between the composition of cast iron and the addition of cerium that the table does not show. In the first place the complete analysis of cast "A" was made in the case of sulfur and phosphorus. No variation was found however and **afterwards** only the untreated specimens and the highest treated specimens were analyzed. If any variation occurred in the intermediate treatments it certainly would be found in the highest treatment. In cast G there is a slight variation in each of the constituents except phosphorus. On the date of this cast the first part of the heat was used for small castings and the last part for some larger castings. Incidentally the charge was changed to obtain the kind of iron desired. An effort was made to get iron of the last composition only but, from the analytical results, it seems that this purpose was not accomplished. This is made more probable by the fact that there is no other such variation. In the case of cast B there was a decided variation in the manganese content. The figure 1.15 per cent is the average of two closely agreeing determinations, 1.118 and 1.183 and the figure .499 per cent is the average of three determinations, .5067, .4834, .5070. The

other constituents of this cast checked. There is only one other variation in manganese and that is in cast G. However in cast G the manganese in the cerium treatment increases rather than decreases so neither of these variations could possibly be ascribed to the cerium. Both are doubtless due to a variation in the charge. There is a variation in cast F in the phosphorus content. The figure .7489 per cent in the table is the average of two determinations, .7146 and .7832 and the figure .9975 per cent is the average of two determinations, .9691 and 1.0260. This variation is slight and since there are no others it could hardly be attributed to the addition of the cerium.

These analytical results then seem to show, without question, that the addition of cerium to cast iron does not vary the percentage of the common constituents.

MICROPHOTOGRAPHS

It was suggested above that even tho the chemical analysis of the iron remained the same it is not safe to assume that there was no change in the properties of the iron. Any change in properties which can not be explained by analysis may be due to a change of crystalline form within the metal, a variation in the sizes of the crystals or it may be due to a new compound within the metal which however does not change its analysis. The structure of cast iron is determined very largely by the percentages of free and combined carbon and also by the condition in which they exist. In an effort to detect any possible variation in the structure of cast iron due to the addition of the cerium all-oy microphotographs were taken in considerable numbers.

The Work Of Photographing.

The marked bars, described under general method

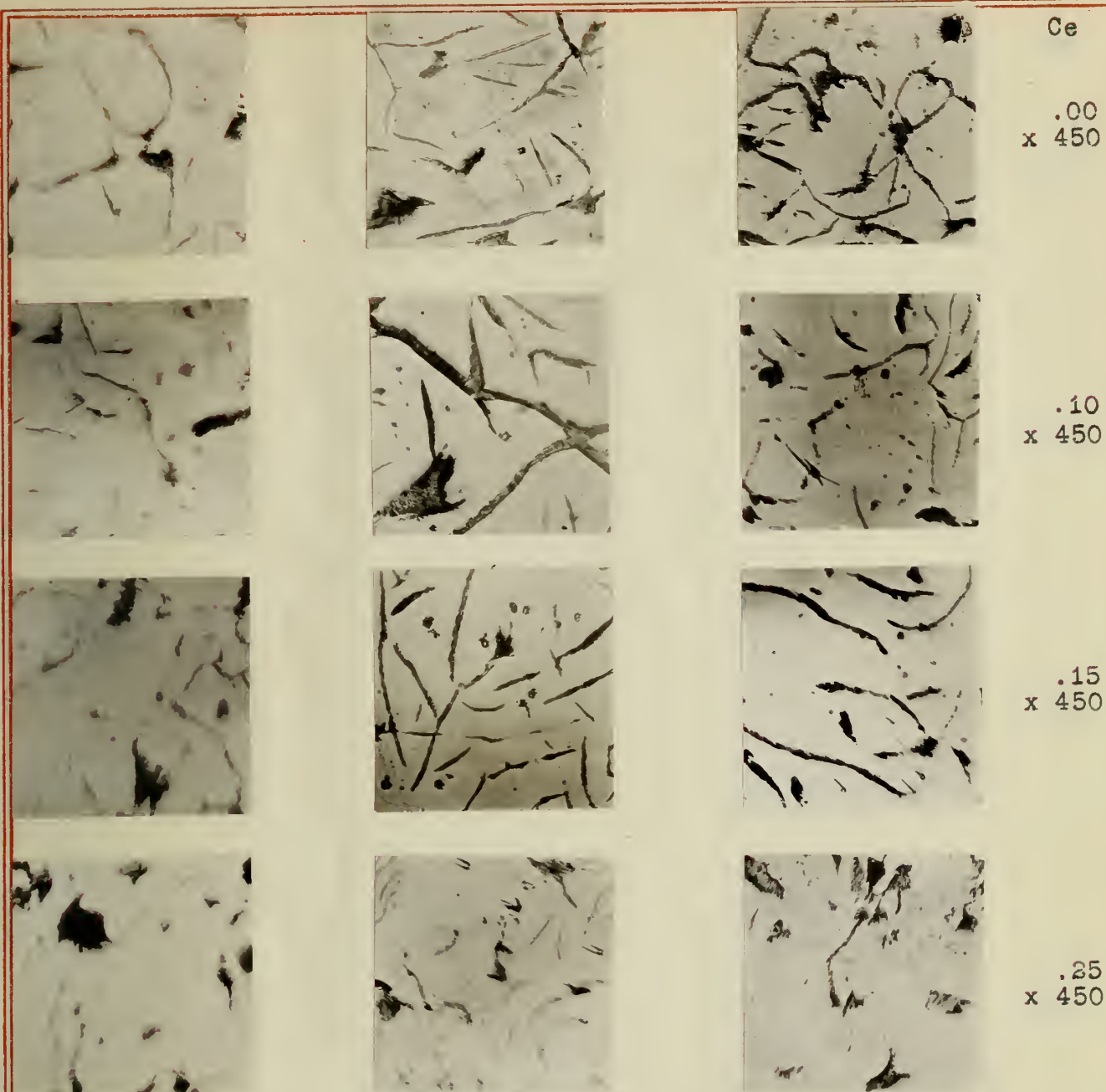


PLATE I

Cast A				Cast B				Cast C				o/o	Ce
.00	.10	.15	.25	.00	.10	.15	.25	.00	.10	.15	.25		
.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00		Ce
1.50			1.40	2.50			2.50	2.30			2.20		G C
1.80			1.80	2.20			2.10	1.80			1.70		Si
.37			.37	1.15			.50	.32			.40		Mn
.12	.12	.11	.11	.07			.07	.11			.10		S
.47	.53	.47	.50	.20			.24	.32			.29		P
2425	3400	2425	3030	2481	2344	2275	2568	2880	2133	2175	2500		C B R
228	228	228	228	169	163	162	169	204	156	178	157		Brin H
30.3	30.3	29.8	30.1	25.5	26.1	25.0	27.1	26.0	27.6	28.6	27.8		Sclr H

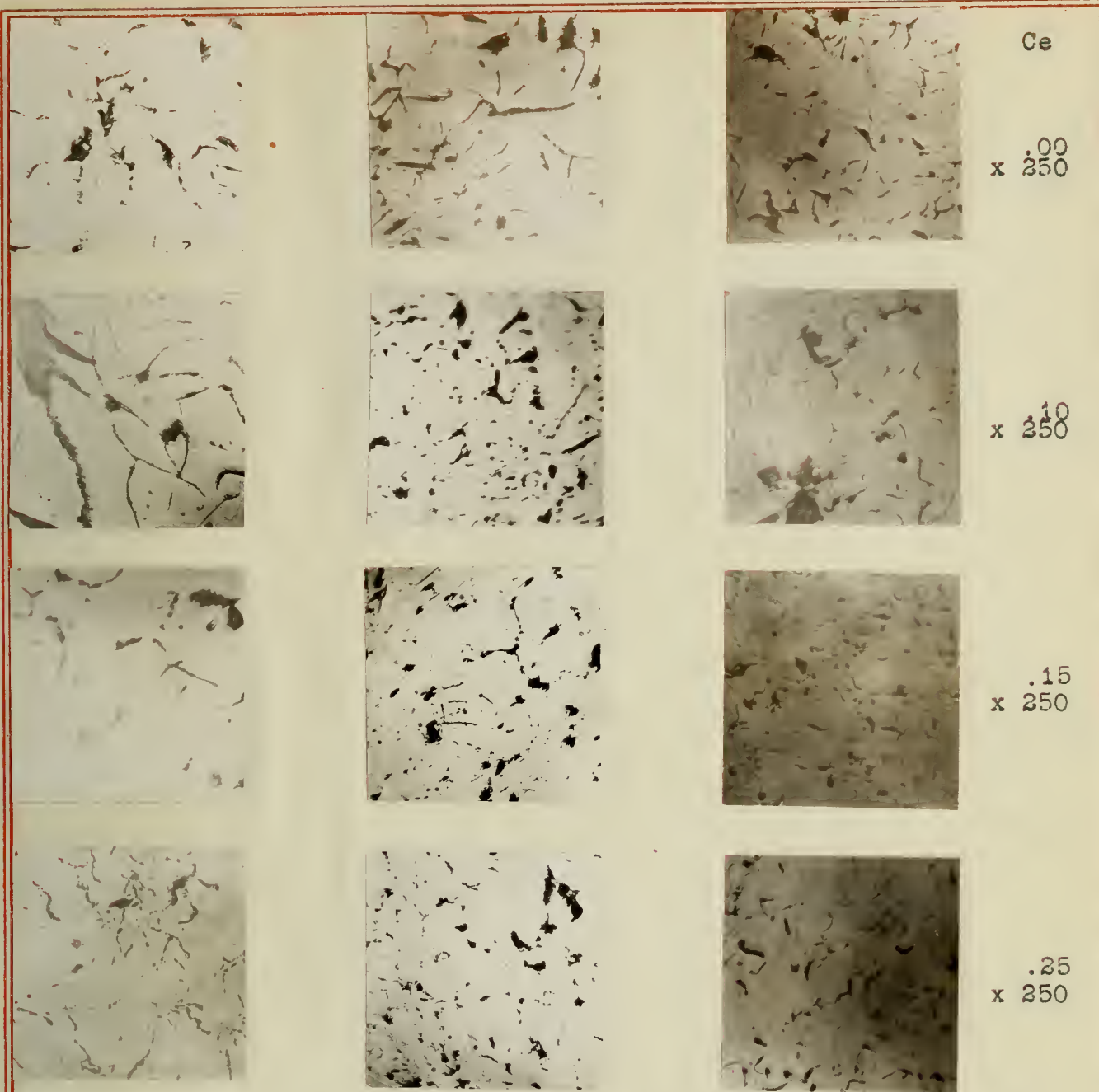


PLATE II

Cast E				Cast F				Cast G				o/o	Ce
.00	.10	.15	.25	.00	.10	.15	.25	.00	.10	.15	.25		
.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00		Ce
1.90			1.90	2.80			2.60	2.80			2.60		G. C
1.90			1.70	1.70			1.60	1.70			1.80		Si
1.40			1.30	.28			.33	.41			.70		Mn
.07			.06	.09			.09	.10			.09		S
.31			.32	.75			1.00	.23			.24		P
2890	2337	2325	2787	3150	2425	2212	2566			3112	2750		C B R
174	152	149	160	183	163	176	203	191	165	195	189		Brin H
25.4	26.4	25.8	26.0	26.4	28.0	26.9	28.5	28.9	25.5	30.2	30.3		Sclr H

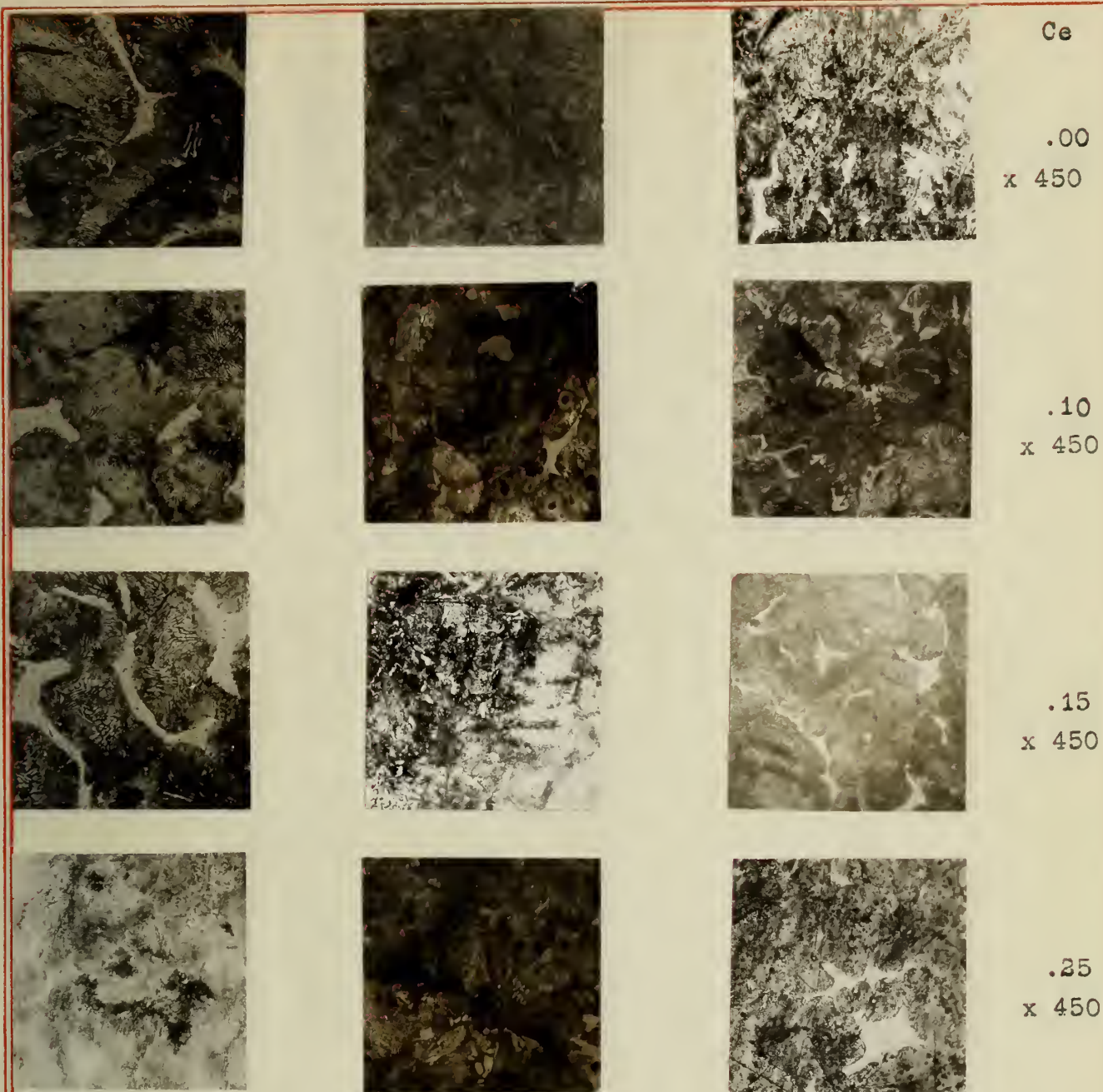
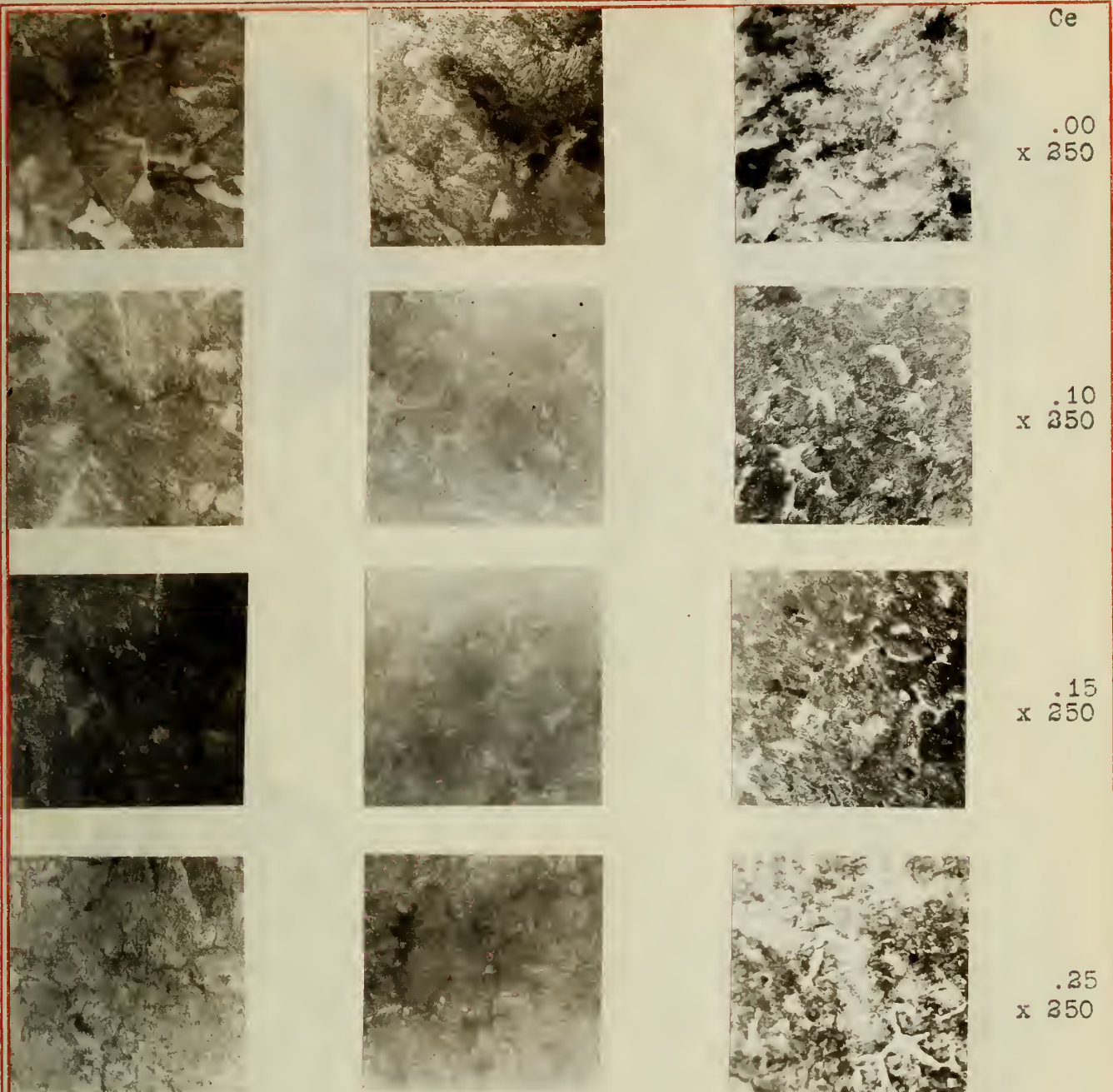


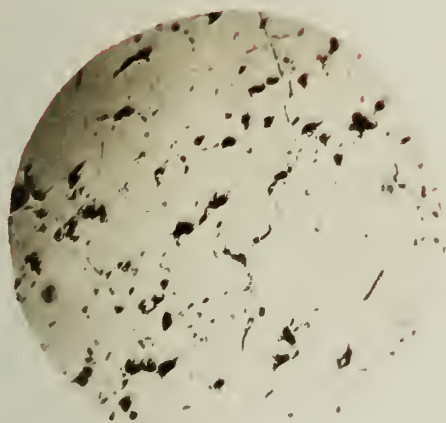
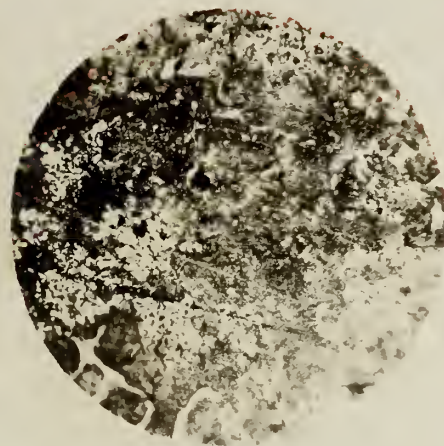
PLATE III

Cast A				Cast B				Cast C				o/o	Ce
.00	.10	.15	.25	.00	.10	.15	.25	.00	.10	.15	.25		
.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00		Ce
1.50			1.40	2.50			2.50	2.30			2.20		G. C
1.80			1.80	2.20			2.10	1.80			1.70		Si
.37			.37	1.15			.50	.32			.40		Mn
.12	.12	.11	.11	.07			.07	.11			.10		S
.47	.53	.47	.50	.20			.24	.32			.29		P
2425	3400	2425	3030	2481	2344	2275	2568	2880	2133	2175	2500	C	B R
228	228	228	228	169	163	162	169	204	156	178	157	Brin	H
30.3	30.3	29.8	30.1	25.5	26.1	25.0	27.1	26.0	27.6	28.6	27.8	Sclr	H



Cast E				Cast F				Cast G				o/o	Ce
.00	.10	.15	.25	.00	.10	.15	.25	.00	.10	.15	.25		
.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00		Ce
1.90			1.90	2.80			2.60	2.80			2.60		G. C
1.90			1.70	1.70			1.60	1.70			1.80		Si
1.40			1.30	.28			.33	.41			.70		Mn
.07			.06	.09			.09	.10			.09		S
.31			.32	.75			1.00	.23			.24		P
2690	2337	2325	2787	3150	2425	2212	2566			3112	2750		C B R
174	152	149	180	163	163	176	203	191	165	195	169		Brin H
25.4	26.4	25.8	26.0	26.4	28.0	26.9	28.5	28.9	25.5	30.2	30.3		Sclr H

PLATE IV



Cast F
x 250
0.4 o/o Ce

Cast G
x 250
0.6 o/o Ce

of treatment were broken on a transverse testing machine and samples for microphotographs sawed from the upper end. One sample was prepared from each treatment as arranged in the index of samples. These samples were polished until scratches visible to the naked eye were practically all removed and then a microphotograph taken of both the etched and unetched structures. The time of exposure and details of developing and printing were determined by the camera, strength of solutions and so forth. The magnification, percentage cerium treatment, chemical analysis and results of physical tests are shown on plates I-IV inclusive. The microphotographs of casts A, B, C, are at a magnification of 450 diameters and those of E, F, G, at 250 diameters. These casts are arranged side by side with increasing cerium treatments from top to bottom. In cast "F" a .4 per cent cerium treatment was also made and in cast "G" a .6 per cent cerium treatment. These pictures are shown on plate V. An examination of these microphotographs shows no regular variation of any kind in the structure of the iron. Then if the addition of cerium to the iron has caused a change in its properties, this change is so minute that it is not evidenced by the microphotographs and must be looked for by various physical tests.

PHYSICAL TESTS

Whatever the results of the two investigations described above the ultimate conclusions must be based upon the physical tests since it is really the physical behavior of the metal which determines the ultimate value of the material. The analytical work and the microphotographs serve only as indications of what may be expected and as a possible means of controlling

the physical properties should any variations be found. In trying to solve this problem various physical tests were made including transverse breaking tests, tensile and hardness tests. After the marked bars had been broken on the transverse strength testing machine as previously described (P. 21), the lower half of the bar was machined to form tensile test specimens 4 inches long, 1 inch in diameter at both ends, threaded with standard threads for 1 inch from each end and turned down to a diameter of .8 of an inch for 1 1/2 inches at the centre. The samples for Brinell and scleroscope hardness tests and the analytical samples were obtained from the upper ends as well as the samples for photographing as described above. The hardness samples were about 1 inch in thickness and the metallographic samples about 1/4 of an inch.

The Transverse Test.

The transverse tests on the specimens used were made in the Applied Mechanics laboratory of the University of Illinois. An Olsen testing machine with an automatic recorder drawing the load-deflection diagram was used. The scales used were one inch to one thousand pounds of load and one inch to one tenth inch deflection. The load was applied to the bar, midway between supports fourteen inches apart, by means of a hand wheel, gear train and screw.

Tensile Test.

The tension tests were made on a Riehle 100 000 pound, power driven, testing machine. The standard specimen was screwed into the grips, one of which was clamped in an ordinary friction grip and the other attached to a ball joint so that the load was always applied along the axis of the specimen. The load was applied as slowly as possible and the load at rupture record-

ed. As the elongation and reduction of area in cast iron specimens are so small the recording apparatus was not used.

Hardness.

The scleroscope hardness tests were run with one of the late models of the instrument and at least three determinations and usually from five to seven, were made on each specimen. The results recorded were the average of these readings.

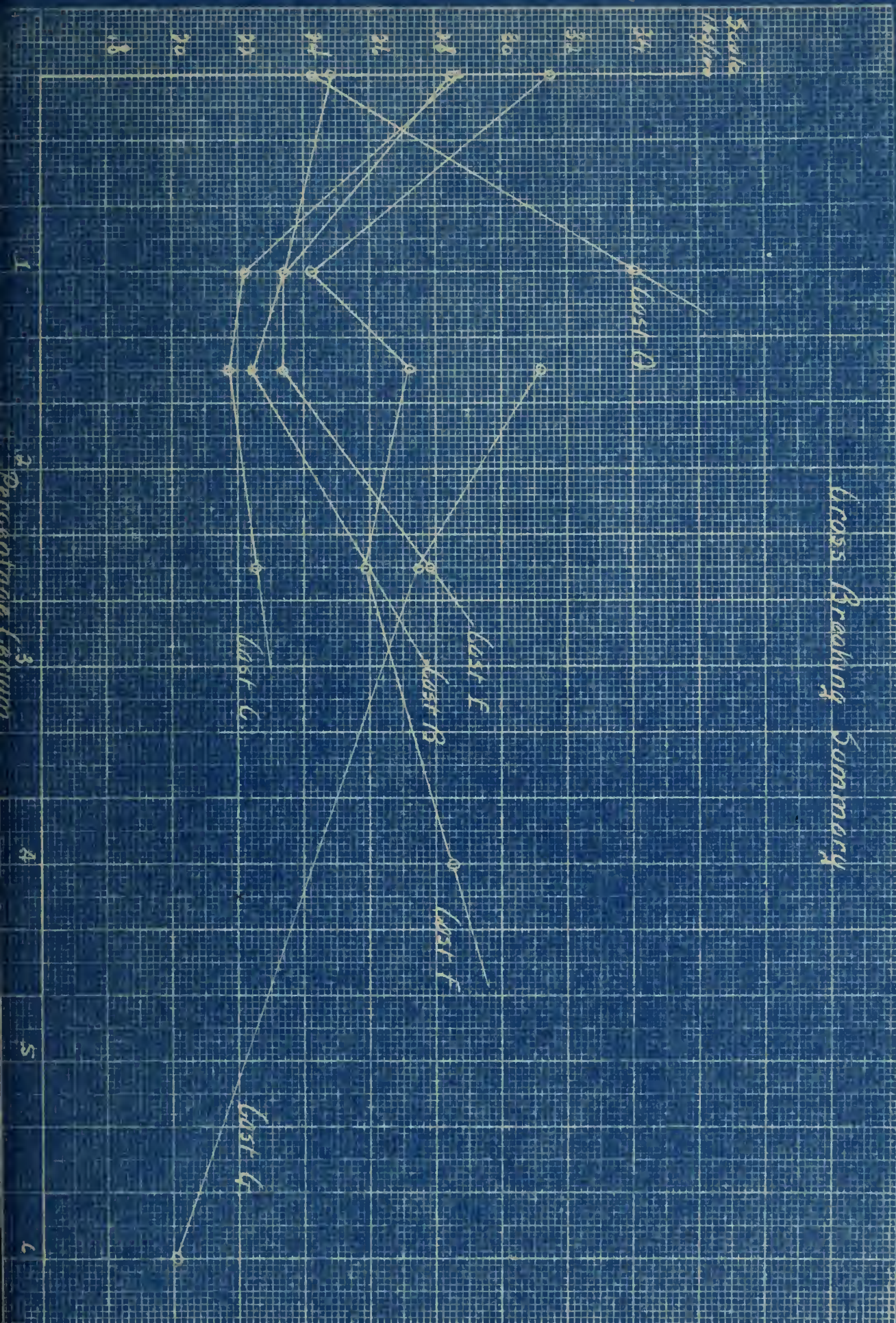
The Brinell hardness tests were made on a standard model of Brinell testing machine made by the Pittsburg Instrument and Machine Company. The width of depression made in the specimen was measured with a Tineus Olsen measuring telescope and checked on a Bausch and Lomb microscope having a micrometer attachment on the mechanical stage.

The results of the above described tests are represented graphically on graphs 1 to 11. By an examination of these graphs it will be seen that general summaries have also been drawn up in graphical form. These same results (except tensile strength) are given in tabular form on plates I-IV. The physical tests were not as satisfactory as was desired. Too many specimens showed defects which either rendered the cross-breaking and tensile data unreliable or eliminated them entirely. The hardness tests furnish the most reliable data on these specimens and of the two hardness tests employed the data obtained with the Brinell machine is undoubtedly superior to that from the scleroscope.

A consideration of the cross-breaking data shows that in the one case where consecutive sets of sound bars were obtained (cast A) a marked increase in transverse strength is

Cross Breeding Summary

(72 305)



Table

and Roundel/ins

Table of 1st memory

Unit

Unit

Unit

(731)

Stereoscope Address Summary

Scale

32
31
30
29
28
27
26
25
24

1

2

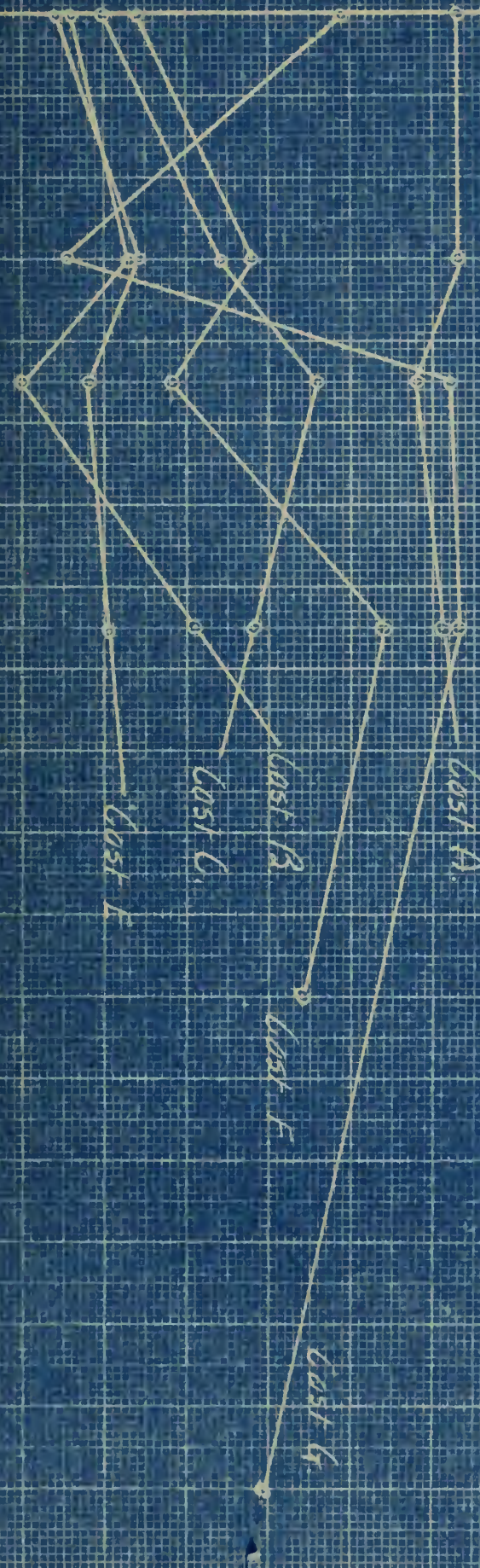
3

4

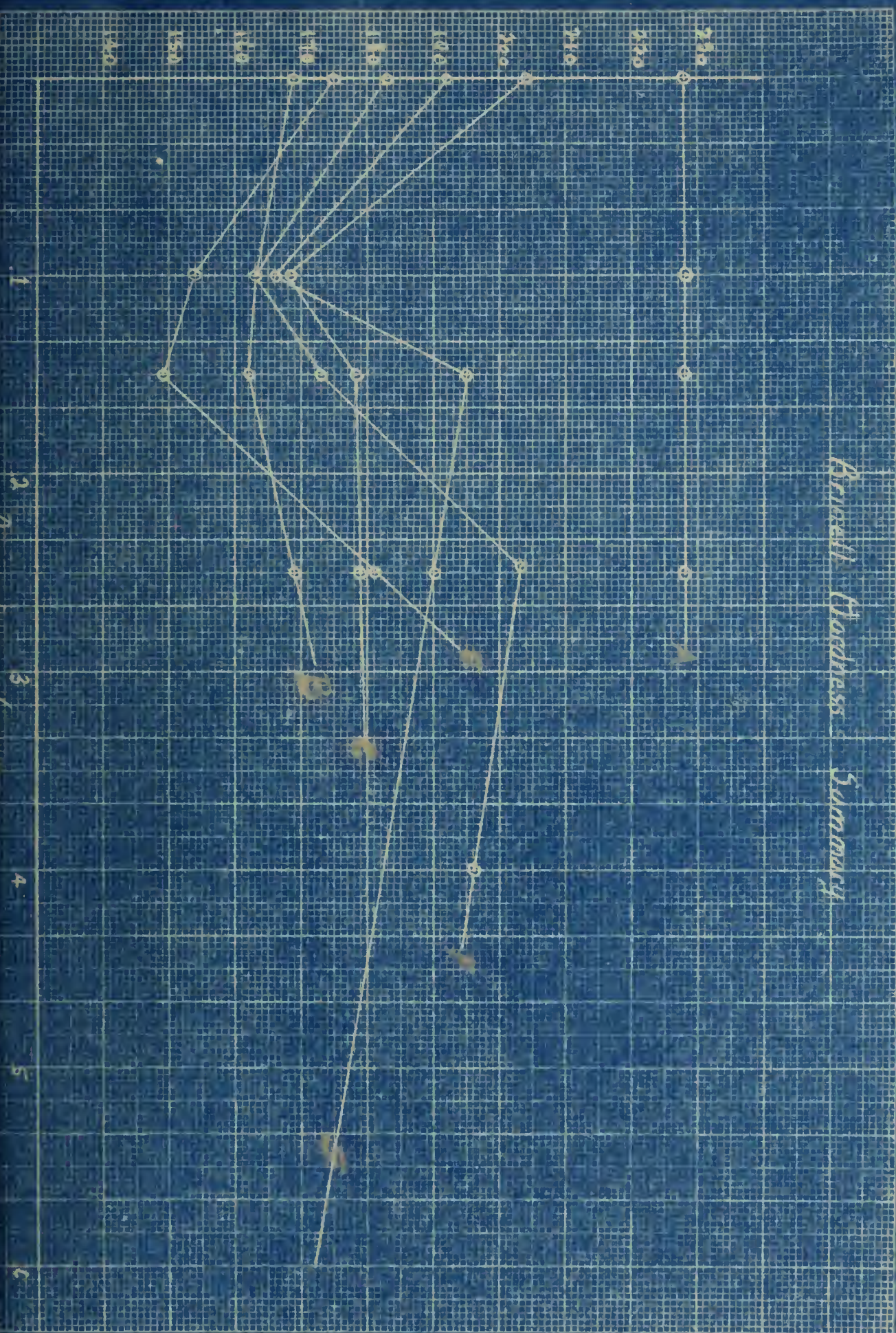
5

6

Percentage Devium



Artificial Grassiness Summary



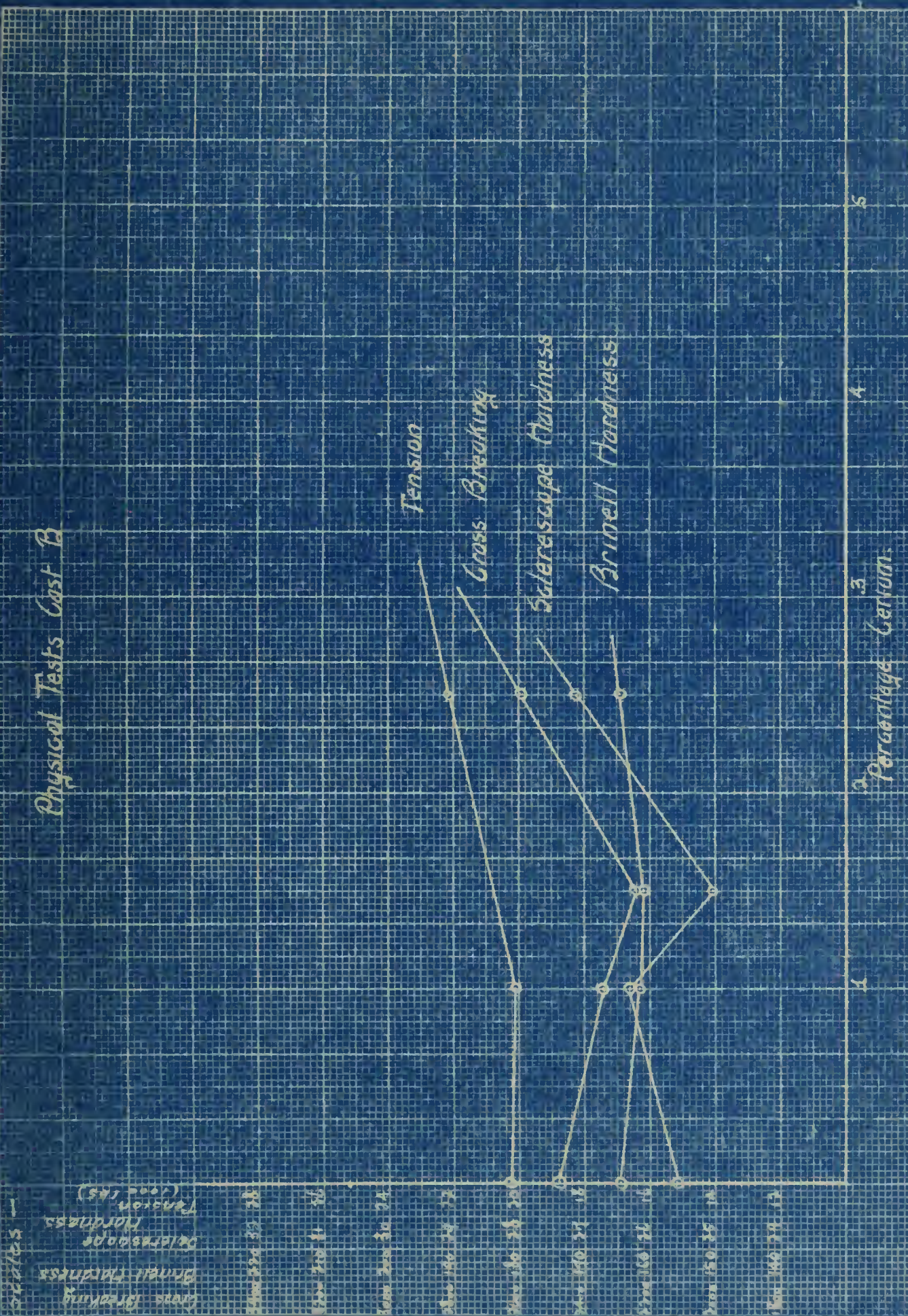
100

Physical Tests Cast B

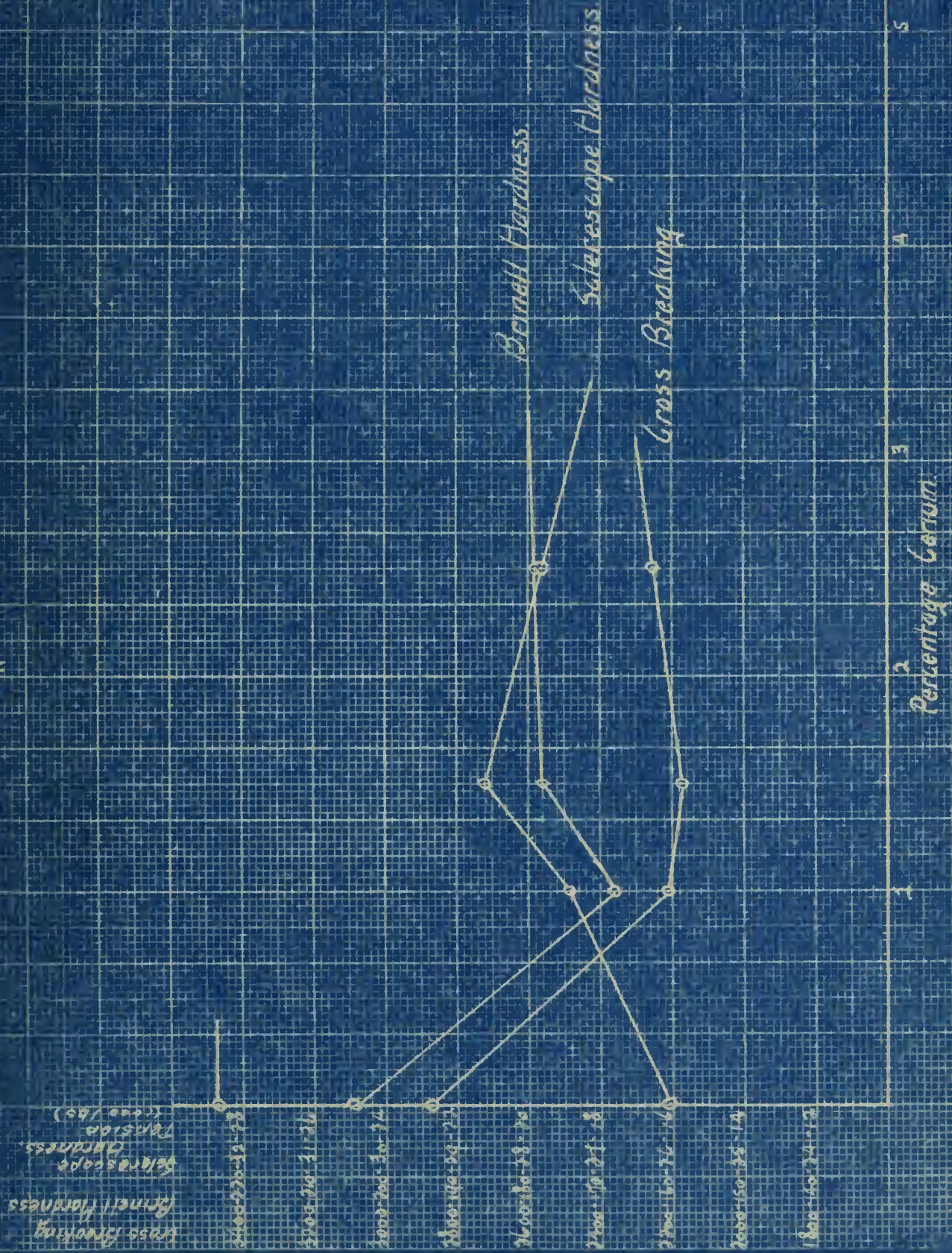
Tension (Cool Test)
 Hardness
 Brinell Hardness
 Rockwell Hardness
 Charpy Hardness
 Impact Hardness
 Tension (Hot Test)
 Tension (Cold Test)
 Tension (Hot Test)
 Tension (Cold Test)
 Tension (Hot Test)
 Tension (Cold Test)

Tension
 Gross Breaking
 Scleroscope Hardness
 Brinell Hardness

Percentage Carbon



Diagnostic Tests Lab 6



500 lbs -
 Gross Breaking
 Punnett Hardness
 Scleroscope
 Hardness -
 Tensile
 Strength

Physical Tests Cast A

4000 3500 3000

2500 2000 1500

1000 500 0

0 100 200 300

400 500 600 700

800 900 1000 1100

1200 1300 1400 1500

1600 1700 1800 1900

2000 2100 2200 2300

Gross Breaking

Punnett Hardness

Scleroscope Hardness

Percentage Carbon

5

4

3

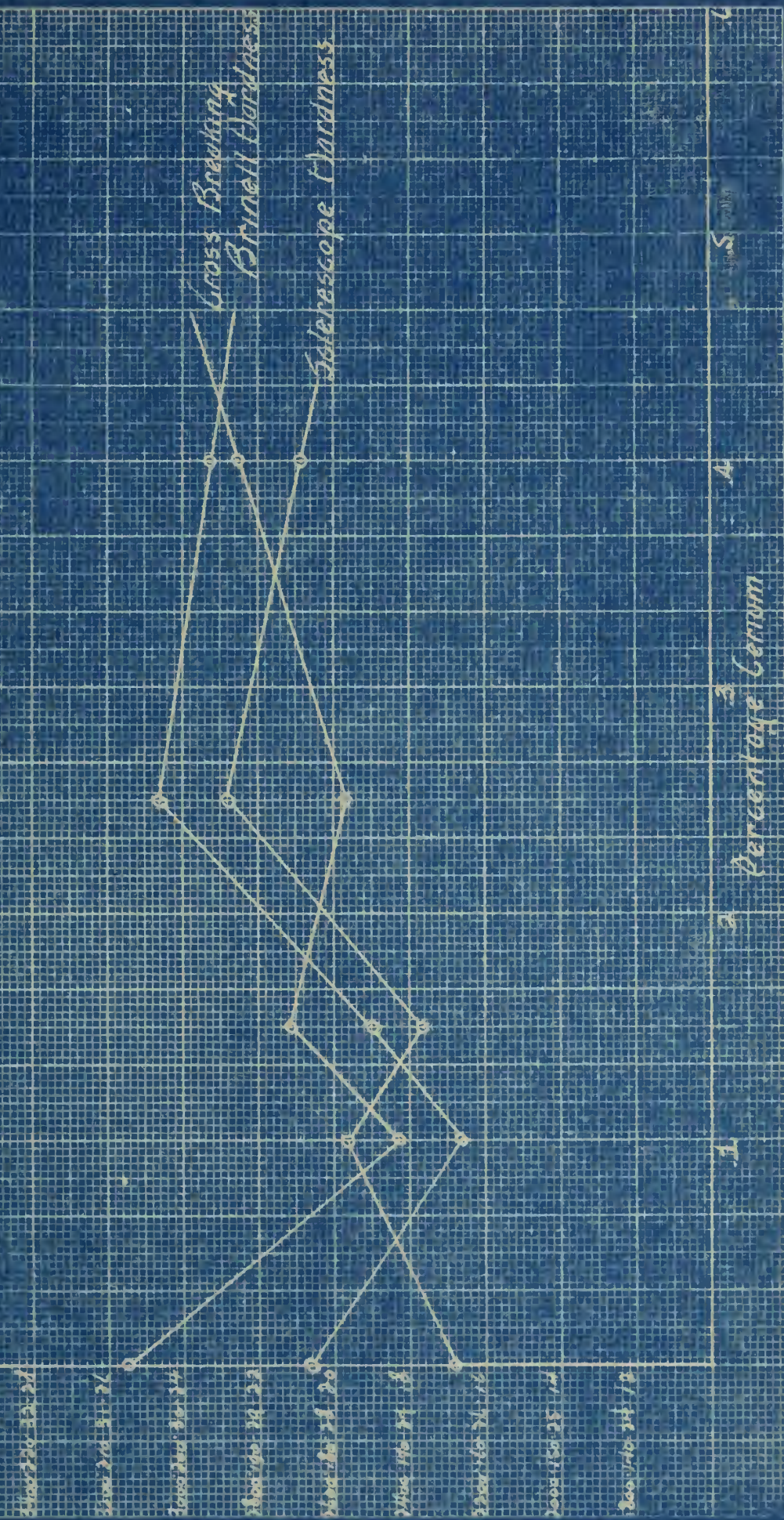
2

1

0

Physical Tests Cast F

Gross Bending
 Brinell Hardness
 Rockwell C
 Shore D
 Tension Test



Scales -

Handwriting
 English
 Arithmetic
 Spelling
 Reading
 Grammar
 History
 Science
 Geography
 Civics
 Health
 Music
 Art
 Physical Education
 Social Studies
 Foreign Languages
 Miscellaneous

Physical Tests Cost of

Physical Tests

Cost of

Physical Tests

Cost of

Physical Tests

Cost of

Physical Tests

Cost of

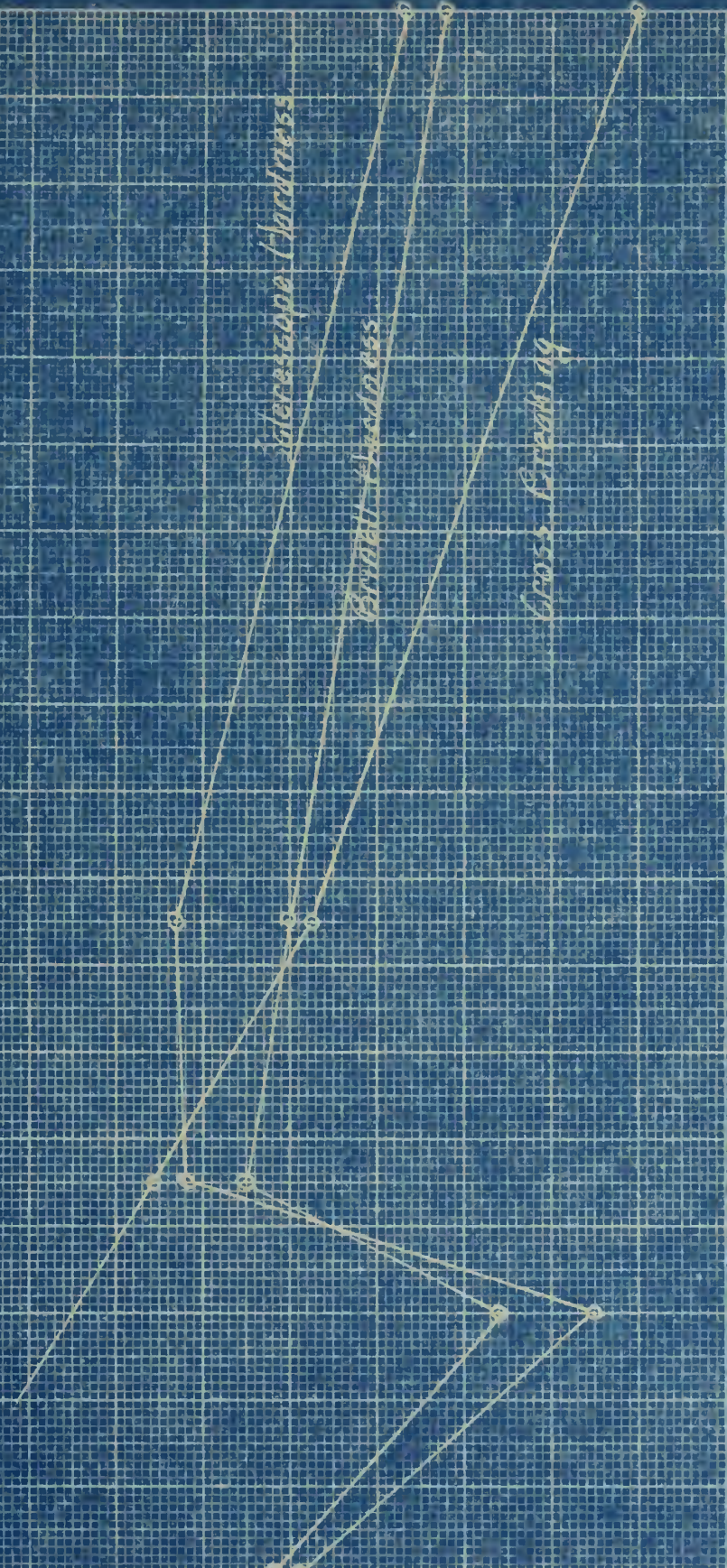
Physical Tests

Physical Tests

Cost of

Physical Tests

Percentage of



500/05-

Comparative Average Grades

Gross Breaking
Brinell Hardness
Scleroscope Hardness
Tension lbs

24000 24 28
22000 20 31 26
2000 200 30 24
2100 180 24 22
1800 160 23 20
1600 140 21 18 0
1400 120 21 16 16
1200 100 20 14 14
1000 80 19 12 12

A - Gross Breaking
B - Scleroscope Hardness
C - Brinell Hardness

G

B

A

A

S

C

Percentage German

1 (7 x 2)



evidenced, the strength increasing from 2750 pounds per square inch to 3400 pounds upon the addition of 0.1 per cent cerium. The tensile test on the same specimens showed a similar increase from 24500 to 27100 pounds per square inch. Sound specimens were available from casts E, F, and G for the turning of tension specimens but because of delay at the machine shop the data has not been available. In a general way these tests indicate that, defects due to foundry practise being eliminated and having the metal treated hot enough to allow proper mixing without chilling the iron, beneficial results are obtained by the use of cerium.

(Note. The graphical data on the tension tests for cast A is not correct due to the fact that it was not calculated to pounds per square inch. To obtain the correct value it is necessary to divide the results given on the graph by .504).

The scleroscope hardness tests vary to such an extent and with so much irregularity that it would seem unwise to place any weight upon them as evidence. The data from the Brinell hardness, however, varied fairly uniformly in all except the first cast. In all cases the addition of 0.1 per cent of cerium tends to decrease the hardness number, indicating an increase in tensile and transverse strengths and an improvement in the machinability of the metal. The addition of .15 per cent cerium tends to increase the hardness slightly over the value obtained by the first treatment, while .25 per cent brings the value back to a point near the original figures and amounts of cerium over .25 per cent apparently tend to produce a softer metal. The exception to this data is cast A which was noticeably harder than the other casts. In this cast it is to be noticed that the charge

consisted of part pig iron and part scrap steel, having a low graphitic carbon content. The hardness is probably due to the combined carbon present more than to any other factor and therefore it would be unsafe to attach any particular significance to this increase in hardness.

SUMMARY

To summarize the experimental results, 74 analytical determinations representative of 88 different samples and 528 determinations show no change in the chemical analysis of the iron upon the addition of cerium more than would be expected when working with metal drawn from a small cupola from different taps. This conclusion is strengthened by the fact that the few slight variations that were found occurred with absolutely no regularity. Fifty-two individual microphotographs, representative of 88 samples and 175 photographs show no regular variation in the structure of the iron when treated with cerium. A few microphotographs of Dr. Moldenke's iron, mentioned on page four, were available and it seemed that in one or two instances there was a similarity between some three or four of the photographs of different treatments but this was very uncertain and did not warrant any conclusions. The number of physical tests and the meaning of them cannot be so concisely stated since there were so many defective bars due to foundry practise. On the whole tho the physical tests seem to indicate that the addition of cerium increases the tensile and transverse strengths and makes a softer metal.

With the results of these three investigations in mind, viz., the data from the analytical work and physical tests together with the microphotographs, the merits of the cer-

ium treatment of cast iron can be discussed with at least a certain degree of intelligence and understanding. Whether the cerium acts as a deoxidizer in cast iron or not can not be stated from this work but since there is no evidence to the contrary it probably does. However that is not a part of this problem but only an interesting speculation.

In considering the possibilities of using cerium in this way one of the first points which would be considered by a foundry man would be the cost. Cerium alloyed with 30 per cent iron costs, at the present time (June 1, 1920), \$10.00 per pound with the prices running down to about \$8.00 per pound in quantity lots. At this rate the cost of treating the castings with cerium would amount to $1 \frac{1}{4}$ to $1 \frac{1}{2}$ cents per pound for each .1 per cent of cerium added. It is very evident that, with the close competition prevailing, such an increase in cost would prove prohibitive except in the manufacture of small or especially complicated castings where the selling price is not based on the weight of metal in the casting. This is especially significant since all foundry men know that the properties of their product may be changed by a variation of the common constituents such as silicon and manganese. If a variation in the amounts of these cheaper elements can be made to give the desired product the use of cerium will be eliminated. The way in which the cerium causes a variation in the properties seems to be different from most of the other more common constituents. It increased the tensile strength of the iron and its hardness and at the same time increases its transverse strength. It is an easy matter to get one or two of these variations by means of the ordinary constituents

but difficult, if possible at all, to get a combination of all three. The problem, then seems to warrant further investigation with a view to making use of the process especially in the field of malleable cast iron where the purpose is to make small castings.

CONCLUSIONS

The net result of the whole investigation seems to be as follows.

1. It has been found that the addition of small percentages of cerium to cast iron causes no variation in chemical composition that can be detected by ordinary analytical methods. No trace of cerium is found even when as much as .6 per cent is added.

2. It has been found that the addition of small percentages of cerium to cast iron causes no variation in structure which is evidenced by microphotographs.

3. It has been found that the addition of small percentages of cerium to cast iron causes, (when added under favorable conditions), an appreciable increase in transverse and tensile strengths and produces a softer casting.

4. It has been found that when the beneficial effects caused by the addition of cerium to cast iron are compared to the cost of the cerium that the use of cerium in this way is not an advantage except in rare cases.

SUGGESTIONS FOR FURTHER WORK

If further work is done on this problem more satisfactory results will be obtained by observing the following precautions.

1. Use only very hot metal in making the tests

in order to avoid "cold iron".

2. If possible, carry on the test in such a way that iron for all comparative tests can be obtained from one large ladle and at as near the same time as possible in order to prove definitely whether or not cerium has any effect on the various properties of cast iron.

3. Have the molds made as uniformly as possible; on a jar ramming machine if available; and carefully dried. Under-drying gives badly blown bars and over drying imperfect bars due to crumbling of the molds.

4. Always use previously heated ladles and allow the possible deoxidation products time to escape before pouring the iron.

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